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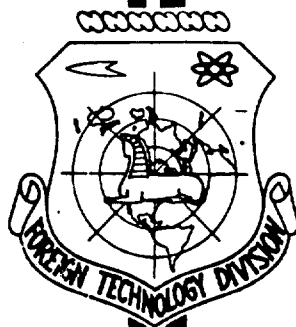
TRANSLATION

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A MATHEMATICAL THEORY OF STABLE LYOPHILIC COLLOIDS

By

B. Deryagin and M. Kusakov

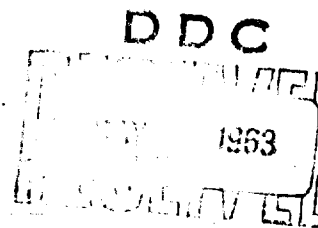
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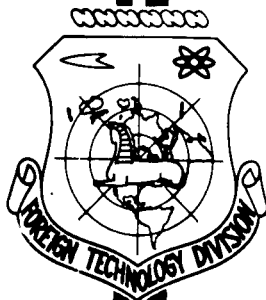
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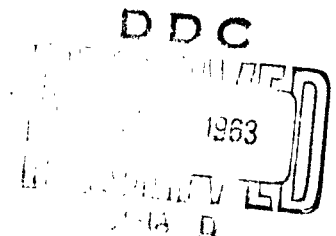
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FOREIGN TECHNOLOGY DIVISION
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EXPERIMENTAL STUDY OF SURFACE SOLVATION IN DEVELOPING
A MATHEMATICAL THEORY OF STABLE LYOPHILIC COLLOIDS¹

(Anomalous properties of thin liquid layers. V)²

B. Deryagin and M. Kusakov

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Mathematical and Natural Sciences, 1937, 1119-1152

Current concepts of surface and colloidal particle solvation are critically reviewed, as are methods for studying such phenomena. This is followed by a new quantitative procedure for determining solvation, which relates it to the disjoining effect of thin layers of liquids discovered and studied in previous reports of this series.

In the present report, a new, more convenient method is described for measuring the thickness and disjoining effect of thin layers, for the case where these are boundary layers between a lyophilic solid and a gas bubble.

Further observations are reported on the nonequilibrium state of such wetting films.

Experimental data are given which establish an equation for the state of a solvate layer expressing the equilibrium pressure (disjoining action) of this layer as a function of layer thickness, for both

aqueous and nonaqueous media.

The effect of electrolytes on the thickness h of a solvate film is described, as well as the effect of surface-active substances on a vaseline oil film solvating the surface of steel.

A theory of micelle interaction is given which takes account of the disjoining effect produced by thin layers of the dispersion medium separating adjacent surfaces.

Finally, these last calculations are used to develop a theory of slow coagulation and stability of colloids in disperse systems.

1. Introduction

In surface solvation of colloidal particles, as it is generally understood, such particles are 'bound' by the surfaces of adjoining layers in a liquid dispersion medium. This concept is used consistently to explain the more important properties of lyophilic colloids - among these, so basic a property as aggregative stability (Ref. 1) in the sol state.

The solvation concept thus appears to be one of major significance, yet it still lacks a firm basis, in rigorously verified experimental observations. Moreover, it has never been given a precise physical definition and therefore remains vague. In fact, different authors have attributed widely differing meanings to this concept.

If the situation is unsatisfactory, the principal reason why this is so, as we see it, is that up to the present time there has been practically no attempt made to use a direct experimental approach, in a study concerned specifically with the properties of solvate layers formed on

macrosurfaces. As a result, there has been a tendency to obtain information regarding these properties by studying the general, rather than specific, behavior of colloidal systems.

The situation is reversed, and far more satisfactory, in electrokinetics. It is mainly for this reason that the properties of lyophobic colloids have been successfully interpreted in the light of electrokinetic phenomena.

The entire vast literature on solvation of colloids indicates that studying lyophilic colloidal systems as a whole does not lead to any unambiguous and reasonably accurate conclusions as regards thickness, structure and properties of solvate layers. Such conclusions could not be derived from theory alone, even where an adequate theoretical basis exists. An Einstein formula is available, to cite one instance, for estimating the quantity of dispersion medium participating in the motion of particles from measurements of sol viscosity. Yet in 25 years since the first attempts in this direction not enough definitive data have been obtained on the thickness of solvate layers in lyophilic systems.

The same can be said of the various methods for studying bound water in hydrophilic colloids (Ref. 3). If the results of such studies are difficult to interpret, the principal hindrance is lack of information. The total surface of dispersed particles, in lyophilic systems, is usually unknown; nor do we know the exact proportion of the liquid bound inside the micelles. Still, studies of bound water (also, of viscosity) in lyophilic systems give valuable indications as to the nature of changes in volumetric properties of liquids taking place in the solvate layers of a micelle-bound dispersion medium.

Nevertheless, the study of colloids, especially the lyophils, calls with increasing urgency for exact information on the thickness and

properties of solvate layers. Such information is most essential in developing a quantitative theory of colloid stability. These much needed data have not been made available, however, nor has the very concept of solvation been clearly defined. As a consequence, attempts at explaining some of the basic properties, above all the stability of colloids, amount to little more than vague verbiage, for the most part devoid of exact physical meaning. A case in point is the concept first proposed by Bungenberg de Jong (Ref. 4), and later so generally accepted that it has been introduced into some textbooks on colloidal chemistry (Ref. 5). According to de Jong, the diffusivity, or washout, of a solvate transition layer can be the sole factor determining the aggregative stability of lyophilic systems, since it eliminates adhesive forces. No sound basis for this proposition has ever been suggested by anyone. The idea, rather nebulous to begin with, is in fact incorrect, as will be shown below (see Section 8). A simple mathematical computation makes it evident that the washout of a solvate layer, far from contributing to the stability of a colloidal (or a dispersed) system, will in effect lower this property.

One more rather common misconception should be cleared up, if our problem is to be correctly posed, before we go on to the description of methods developed by us for investigating solvate layers. Different investigators have taken one or another property as the basis for characterizing solvate layers and their thickness. As a result, they have arrived at widely divergent thickness values. And this is not all. The exact meaning of 'thickness' should be more closely defined. It would seem more logical, in this case, to speak not of solvation in general but of "specific properties" and manifestations characterizing solvate layers, which depend on the surface upon which these layers have been formed. It must be kept in mind (Ref. 6) that the effect of

separation surface may vary from one property to another, in its scope of penetration into the depth of the liquid; hence, different properties can be localized in layers of unequal thickness. Finally, the thickness itself depends on the particular criterion (degree of deviation) used to determine whether a given portion of the liquid belongs to the solvate layer. In other words, the extent to which some property deviates from normal (corresponding to the entire volume of liquid).

The most important property of colloidal systems is stability -- an indispensable condition of their very existence. Therefore the particular property that determines the aggregative stability of such systems is the logical choice for the basic criterion characterizing a solvate layer.

2. Cleavage as the criterion of solvation

What property is that?

We shall make a basic assumption (Ref. 7) that in a general case the stabilizing effect of solvate layers is due to cleavage - or 'disjoining action,' as one of us called it (Ref. 8) - first discovered and later studied by B. Deryagin and E. Obukhov (Ref. 9).

This effect consists in the following. The solvate layers of two surfaces (either flat or convex, as in colloidal micelles) come in contact and are superimposed. On sufficiently close contact a pressure develops, which is a single valued function of the distance between the these surfaces, and not only opposes closer contact but actually tends to move them farther apart. Thermodynamically, the cleaving (disjoining) pressure is identified with the state of equilibrium of the liquid layer confined between the above two surfaces, being drawn together in an infinitely slow reversible process. The cleavage, therefore, has nothing in common with the resistance to the thinning of the liquid layer, which is due to viscosity, and becomes apparent as the liquid

flows out of the clearance between the two surfaces. The cleavage is caused by molecular forces of attraction acting between the micellar surfaces and the molecules of a solvate layer. This attraction exceeds the molecular forces of attraction acting between mutually approaching (micellar) surfaces.

It was shown earlier (Ref. 10) that, because of cleavage, the free surface energy of a system in which thin layers are present will depend on layer thickness. To be specific, it will increase as the equilibrium thickness of these layers decreases.

Such an approach to solvation phenomena offers the following advantages.

- 1) Its basic concept of disjoining action (cleavage) is both clearly defined and quantitative (since the cleaving effect is interpreted as a function of layer thickness).

- 2) It relates cleavage directly to the stability of colloidal systems (as well as to their other important properties such as swelling or peptization). This relationship, as will be shown in Sections 8 and 9, provides a basis for a quantitative mathematical theory of stability and coagulation of colloids.

- 3) It makes possible direct quantitative measurements of cleavage on macrosurfaces of any nature.

- 4) The cleaving action, corresponding to the equilibrium states, can be treated thermodynamically. (This was verified directly in our experiments with macrosurfaces).

- 5) The cleavage provides a measure of the intensity of molecular attraction between the solvated and solvating phases. It follows that our concept does not disagree with the commonly accepted views on solvation but rather develops these views, making them more precise.

These assertions are further clarified and substantiated by the following calculation. Let the free energy of a system consisting of two bodies, 1 and 2 (two micelles), and a dispersion medium 3 (Fig. 1), be represented by a sum \sum , which is the total energy of all the molecules in the system paired in every possible combination. Each term of this sum refers to a particular pair of molecules, expressing the energy of their interaction. The latter will depend on the nature of the two molecules and the distance separating them. On a similar assumption is predicated the classic theory of capillarity developed by Laplace and Gauss.³

Let the molecules contained in the first body be denoted by a, those in the second body by b, and those of the dispersion medium by c. It is obvious that the c molecules will occupy the portion of the total volume of the system which remains after subtracting the volumes 1 and 2 of both bodies (micelles). This must be kept in mind when computing the sum \sum . If this consideration is ignored and, in calcu-

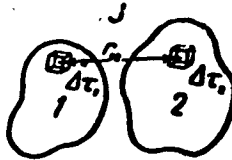


Fig. 1. Calculating particle interaction in a dispersion medium

lating the energy of interaction for all molecules, the dispersion medium is assumed to fill the entire volume of the system, a definite error will result as additional terms are introduced into the sum. Under such an assumption, volume 1, for instance, will be filled both by the a molecules, which are actually found there, and by the c molecules, present in the same concentration as in the dispersion medium.

(While consistent with Dalton's law, this is of course impossible in the case of condensed phases, except in terms of purely formal reasoning).

The above error is however easily corrected, by introducing fictitious molecules c' into volumes 1 and 2, in a concentration equal to that of the c molecules. To these additional molecules a particular property is attributed; namely, that the respective energies of interaction, for a c' or a c molecule with any other kind (a , b , c or c') - the distances being equal - will differ only in sign. In other words, the energy of a c molecule interaction with any other kind (including a c' molecule) will remain the same in absolute value but will acquire an opposite sign if the c molecule is replaced by a c' molecule. By virtue of satisfying this condition, the introduction of fictitious molecules c' into volumes 1 and 2 will compensate for the above error.

The same condition also makes it possible to replace two interacting c molecules by two c' molecules, keeping the same distance between them, without changing either the amount or the sign of interaction energy.

The total free energy of the system can therefore be expressed as a sum \sum' of interaction energies of all molecules. The latter are subdivided into the following groups:

- 1) molecules a filling volume 1;
- 2) molecules b filling volume 2;
- 3) molecules c filling the entire volume of our system, including volumes 1 and 2 and the dispersion medium;
- 4) molecules c' filling volume 1;
- 5) molecules c' filling volume 2.

Let us examine portion \sum_{12} of the free energy of the system that will undergo a change when the position of bodies 1 and 2 relative to each other is varied while their shapes remain the same. This portion

of the total energy can be identified as potential energy mutually possessed by both bodies.

It is obvious that in order to obtain the mutual energy of the two bodies \sum_{12} it is necessary to discard those terms of the sum \sum_{12} that remain unchanged as the positions of bodies 1 and 2 vary. Among these will be all terms expressing the energy of c molecules (3rd group) interacting with one another.

Similarly, the sum of terms expressing the energy of all molecules a (1st group), or b (2nd group), interacting with all c molecules (3rd group) can be discarded, since this sum remains constant if the distance between body 1 (or 2) and the boundaries of the entire system (separating the dispersion medium from the outer medium) remains at all times sufficiently large as compared with the radius of molecular action. The only terms that will be retained are, in the first place, those expressing the energy of all molecules a (1st group) interacting with all b molecules (2nd group). We shall denote the sum of these terms by

$$\sum_{12}^{ab}$$

where the subscripts indicate the placement of molecules (volume 1 or 2) and the superscripts designate the kind of molecules filling the volumes denoted by subscripts. In the second place, the sum \sum_{12} will include terms expressing the energy of molecules c' of the 4th groups interacting with molecules c' of the 5th group. The sum of these terms will be denoted by

$$\sum_{12}^{c'c} - \sum_{12}^{cc}$$

because the energy of interaction does not change when molecules c' and c' are replaced by c and c.

Also included will be a sum of terms expressing the interaction of molecules a (1st group) with molecules c' (5th group), equal to

$$\sum_{ii'}^{ac} = - \sum_{ii'}^{ca'}$$

and, finally, an analogous sum of terms expressing the interaction of molecules b (2nd group) with molecules c' (4th group):

$$\sum_{ii'}^{cb} = - \sum_{ii'}^{bc'}$$

The interaction energy of bodies 1 and 2 in the dispersion medium is thus equal to

$$\sum_{ii'} = \sum_{ii'}^{aa} - \sum_{ii'}^{aa'} - \sum_{ii'}^{cb} + \sum_{ii'}^{cc'}; \quad (1)$$

In the case where molecules a and b are identical, the following equality holds:

$$\sum_{ii'}^{ac} = \sum_{ii'}^{ca} = \sum_{ii'}^{cb}. \quad (2)$$

Equation (2) is self-evident when bodies 1 and 2 are of the same shape and are situated symmetrically relative to some plane of symmetry.

If this condition is not satisfied, then each body 1 and 2 can be subdivided into elementary volumes $\Delta\tau_1 = \Delta\tau_2$, which will be equal to each other irrespective of the particular body to which they are assigned (Fig. 1).

The energy of interaction between any elementary volume of the first body with any elementary volume of the second body will obviously show no variation if molecules a and c exchange place in the two volumes. In other words, this energy will not depend on which body is filled by molecules a and which by c molecules. It follows that the sum of interaction energies of these elementary volumes, which is equal to

$$\Sigma_{::}$$

will not change if the superscripts, i.e., the molecules, are shifted about. This is consistent with equation (2).

Thus, the interaction energy of two bodies (micelles) which have an identical composition and are immersed in a dispersion medium is equal to

$$\Sigma_{::} = \Sigma_{::}^a - 2 \Sigma_{::}^{ac} + \Sigma_{::}^c \quad (3)$$

Expression (3) can be written in the form of a sextuple integral taken over the volumes of both micelles 1 and 2:

$$\Sigma_{::} = N \int_1 \int_1 d\tau_1 \int_2 \int_2 d\tau_2 \{ \rho_a^2 u_a(r_{12}) - 2\rho_a \rho_c u_{ac}(r_{12}) + \rho_c^2 u_c(r_{12}) \} d\tau_{12} \quad (3')$$

where ρ_a and ρ_c are the molar concentrations (densities) of the micellar and the dispersion medium, respectively; $u_{ac}(r_{12})$ is the interaction energy of molecules a and c separated by a distance r_{12} ; $u_a(r_{12})$, respectively u_c , is the interaction energy between two a or c molecules separated by a distance r_{12} ; $d\tau_1$ and $d\tau_2$ are elementary values of the two micelles; N is the Avogadro number.

Identifying molecular interaction with mutual attraction, we shall regard values u_a , u_{ac} and u_c as negative. If the absolute value of u_{ac} is sufficiently large, expression (3') may then become positive; i.e., some energy will have to be expended in order for the micelles, initially separated from each other, to draw together. The existence of cleavage (disjoining action) will thus be demonstrated, in this particular case.

The cleaving action is therefore seen to be related to the strong attraction between the micellar molecules and those filling the

dispersion medium. According to conventional views, this attraction is described as a contributing, and sometimes as a major, factor in the solvation of micelles.

Should molecules a and c exchange their functions - as in phase transition characteristic of emulsions - expression (3) will not change. It follows, to cite one example, that interaction of oil particles in water will be the same as in an oily dispersion medium, although this conclusion is not borne out by general observations on emulsions. The discrepancy can however be ascribed to our basic assumption - accepted also by the classic theory of capillarity - which, as pointed out above, substantially limits the general applicability of our calculations. The latter are cited here mainly because they reveal a close relationship and the conventional concept of solvation.

Resistance to tangential (shear) stresses is often treated as the basic property of solvate layers. It is important in sol viscosity and seems no less essential for the mechanical properties of gels. It is not however a basic property of choice, since it cannot be associated with the many advantages indicated above.

We shall consequently characterize solvate layers by a function expressing the effect of their thickness on disjoining pressure.

3. Cleavage measurement methods

In previous reports on disjoining action (Ref. 10, 9), a method of investigating this effect was described, for the case where a liquid layer is enclosed between two solid surfaces.

The procedure, however, involved a number of difficulties which complicated the work and limited the scope of application. (The surfaces had to be made perfectly flat as well as protected from dust particles, and the like). These inconveniences suggested a need for a simplified procedure. Such a method, it was found, could be developed

if cleavage studies were limited to the particular case of a liquid layer bounded by a solid phase on one side only and by a gaseous or liquid phase on the other. We shall next describe this method, which proved both simple and convenient for use.

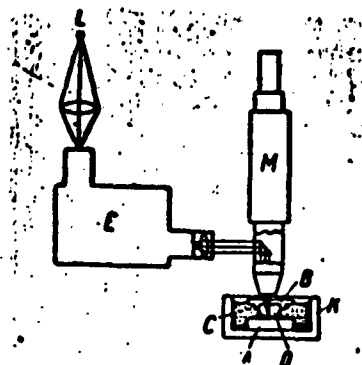


Fig. 2. Installation for measuring the thickness of solvate layers

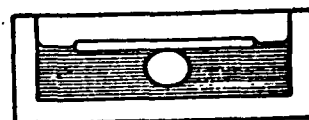


Fig. 3. Free-bubble method used in measuring the thickness of solvate layers

A thin plate (A) prepared from the material taken for investigation -- for instance, glass -- was placed in a flat cell K (Fig. 2). The examined surface had to be sufficiently smooth (as in blown glass) but not necessarily perfectly flat.

An air bubble D was pressed against the surface of plate A. (If the plate was opaque, the pressing was always done from above). A thin transparent plate (B), with a projecting ring C glued onto it, ⁴ was usually employed for this purpose.

In many measurements performed on glass platelets or scales of mica, the procedure was further simplified. A free air bubble was steered toward the underside of a plate immersed in a liquid, and finally settled on it (Fig. 3). This method, however, had its disadvantages. The flattening of the bubble surface in contact with the plate was

determined by the ejecting force, hence it could not be controlled in any other way except by changing the dimensions of the released bubble.

With the aid of a microscope M interference bands were observed (Fig. 2), in the shape of concentric rings running through a wetting film. The film, formed by the liquid filling the cell, was located between bubble D and plate A.

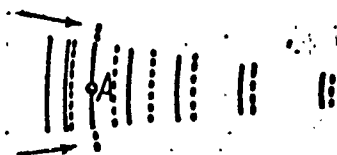


Fig. 4. Displacement of interference rings caused by varying the wavelength of light incident upon a thin film

Illumination was provided by a vertical microscope illuminator. A Fuess monochromator E served as the source of light. The filament of a 200-watt bulb L was projected onto the inlet slit of the monochromator.

It is well known that the position of interference bands (rings) indicates only variations in the thickness of the layer producing the interference; it gives no indications as to absolute thickness values. The reason for this is that when the overall thickness of a layer is changed by any (whole) number of half-waves, the position of interference bands remains unchanged. By using a monochromator, however, we were able to vary in a continuous manner the wavelength λ of light and, simultaneously, to observe a continuous variation of the interference pattern. The ambiguity of thickness measurement data could thus be fully eliminated.

As a case in point (see Fig. 4), let it be assumed that by use of

the monochromator, a wavelength λ_1 has been selected such that it causes a dark interference band (one of the solid lines in Fig. 4) to pass through a point A at which the layer thickness h is of interest to us. Let the wavelength decrease continuously, and let this decrease be accompanied by a continuous displacement of the interference bands (in Fig. 4 the bands are shifted to the right). The next dark band will pass through the same point (i.e., the next darkening will occur) when the wavelength of the illuminating rays becomes equal to λ_2 . The interference bands or, more exactly, rings produced by this wavelength are represented in Fig. 4 as dotted lines.

We can then write:

$$2nh = \left(m + \frac{1}{2}\right)\lambda_1 = \left(m + \frac{3}{2}\right)\lambda_2 \quad (4)$$

where m is some integer and n is the refraction index of the film.

From (4) we find, by eliminating m :

$$\lambda = \frac{\lambda_1 \lambda_2}{2n(\lambda_1 - \lambda_2)} \quad (5)$$

This method is most accurate when h is not too large. If the thickness values are very minute, however, the procedure cannot be rigorously followed. When nh is less than 0.5λ , varying the wavelength over the entire visible range of the spectrum will have no effect beyond a single darkening.

It follows that one equation, at the most, can be derived, of the form

$$2nh = \left(m + \frac{1}{2}\right)\lambda \quad (6)$$

where m and h are unknown. The value m can be found, however, if we first determine, as shown above, a thickness h' corresponding to some other interference band, with a greater path difference, which passes through a neighboring point of the film where the thickness is greater. The value of h is then determined from the relationship

$$2n(h' - h) = m'\lambda - m\lambda = \Delta m\lambda, \quad (7)$$

where Δm is obviously greater by unity than the number of dark bands located between the observed interference bands. It will be noted that the band pattern alone, when observed at some one definite wavelength, does not yet indicate which areas of the field have greater thickness. Hence the ambiguity in determining the sign of differentials ($h' - h$) or Δm . This uncertainty can however be eliminated, by varying the wavelength of the illuminating rays; as the wavelength decreases the bands will shift in the direction of decreasing thickness. The same characteristic enables easy differentiation between the areas of maximum and minimum thickness.

In most of our experiments, the principal objective was to measure the film thickness in areas of its minimum (or maximum) values. The operation, however, involved certain difficulties.

When the wavelength is varied, the areas of average film thickness must be distinguished from those of extreme (high or low) values. In the first case interference bands neither appear nor disappear but move steadily past the area, while in the second case they appear or vanish, but do not shift. Accordingly, in case 1 (see Fig. 4) it is possible, by varying the wavelength, to bring the middle, hence the darkest, portion of the band into coincidence with a given point. In case 2, on the other hand, any given point, encircled by concentric Newtonian interference rings, will invariably coincide with the center of a

dark circle. (This holds for a wide range of wavelengths). But the interference minimum of light intensity (equation 6 holds only for this minimum) will coincide with the dark center only when the wavelength assumes a certain definite value (sometimes a range of values). It follows that the unknown wavelength cannot be determined without measuring light intensity (by a highly specialized photometric procedure). In our measurements, the minimal film thickness involved not a single point but a circle-shaped area (see the photograph of an interference pattern observed in one of our experiments: Fig. 10). This made the problem easier, as will be shown below, in describing one of our techniques used effectively in most cases (barring a few particular thicknesses).

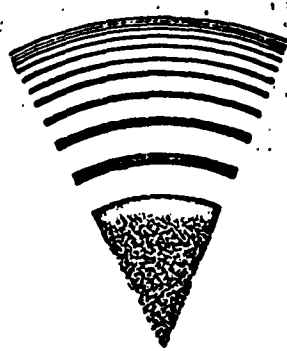


Fig. 5. Interference pattern obtained for the case where the wavelength is not equal to the quadruple thickness of the wetting film in its central portion. Part of the 'border' is visible in the photograph.

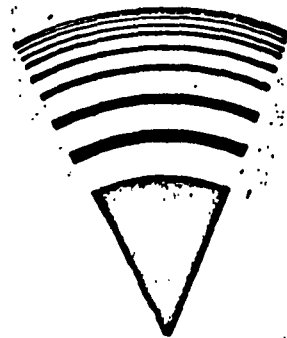


Fig. 6. Interference pattern obtained for the case where the wavelength becomes equal to the quadruple thickness of the film. The 'border' is no longer visible.

Let the unknown minimal layer thickness (when multiplied by the index of refraction) be equal to 0.12λ . For any wavelength λ exceeding 0.48λ , the semi-dark center area corresponding to the

minimum thickness will then be encircled by a much darker 'border'. In it will be located points corresponding to a thickness of $\lambda/4$, or the minimum of light intensity (see Fig. 5). Obviously, by reducing the wavelength until the darker border has vanished, we shall achieve coincidence of the minimum light intensity with the minimum thickness (Fig. 6).

This, evidently, will take place when the wavelength has the value

$$\lambda_0 = 0.48 \mu.$$

Conversely, having determined this wavelength, we can calculate the minimum film thickness by use of formula

$$h_0 = \frac{\lambda_0}{4n}. \quad (8)$$

This method is applicable when

$$0.3\mu > nh_0 > 0.2\mu.$$

Equally effective, in this case, is the analogous 'light border' method. If the adjustment for border disappearance gives a wavelength λ_0' , we have

$$h_0 = \frac{\lambda_0'}{2n}.$$

When

$$nh_0 < 0.1\mu$$

neither method can be used. However, in the particular case where

τ , the following technique is resorted to. A wavelength λ'' is selected at which the interference picture will be equally bright in the center and along the edges, where interference bands are indistinguishable, due to coalescence. From the theory of interference it follows that, in such case

$$n\lambda_0 = \frac{\lambda}{8n} \quad (9)$$

None of these methods, needless to say, is particularly accurate. For high-accuracy data, precise photometric measurements must be taken to determine the relationship between light intensities in the center and those in the areas of maximum and minimum brightness. To this end we now use objective microphotometry performed with the aid of a selenium photocell. As far back as 1914, Wells (Ref. 12) measured the thickness of extremely thin films (such as black soap-bubble spots) by (visual) photometry of rays reflected following interference.

Equilibrium thickness values for various specific pressures were obtained in a simpler way, by taking bubbles of different radii and measuring for thickness the wetting layers separating these different bubbles from a solid surface. Pressure P which the layers are able to withstand, since it is counterbalanced by their disjoining action, can be calculated by applying the first law of Laplace. For nearly spherical, only slightly deformed bubbles, the following formula can be used

$$P = \frac{2\sigma}{r} \quad (10)$$

where r is the bubble radius and σ is surface tension.

The separation surface, in the system 'solvate wetting layer - bubble' is in fact a flat one, therefore the pressures acting upon it from either side are equal. Thus, P in equation (10) indicates simultaneously by how much the pressure in a solvate layer exceeds the pressure in the adjacent volume of liquid. This, essentially, is the measure of a disjoining action as additional pressure by a thin layer, existing in violation of the laws of hydrostatics (law of Pascal).

In our reasoning, we could also follow another, simpler line.

A solvate layer can withstand, without being squeezed out, the bubble pressure greater by the value P than the pressure of the adjacent volume of liquid. This additional pressure can therefore be identified with P .

Thus, by performing measurements on bubbles varying in size, we were able to plot a graph showing the dependence of P on h , for the case of a (nearly) plane-parallel solvate layer.

4. Observation on the nonequilibrium state of a wetting film

Our attempts to obtain a solvate layer in the state of equilibrium by the above method were at first hampered by an interesting phenomenon that merits discussion. When a bubble was pressed against a solid surface, this had to be done slowly and gradually. The condition was not always observed. In such cases the flattened area of the bubble was sometimes large enough to produce a solvate layer profile as seen in Fig. 7 (see insert). Here a photograph of the interference picture obtained for such a case is shown and beneath it, the profile (vertical section) of a solvate layer plotted on the basis of this picture. An unambiguous interpretation of such interference patterns was made possible by applying the following rule: as the wavelength decreases the interference bands (rings) are seen to shift from areas of greater thickness to those of lesser thickness of the solvate layer.

New rings appear where the thickness is maximum and vanish where it is minimum.

The area of minimal thickness is seen to be located not in the center but at some distance from it, encircling the central point. A portion of the liquid layer contained inside this ring had a thickness greater than the equilibrium thickness of the solvate layer -- that is, the thickness value corresponding to the pressure inside the bubble. The thinning of this portion of the liquid proceeded quite

slowly, however, apparently because of the strong viscosity effect hindering the liquid flow through the narrowest areas. (Viscosity, in this case, may have been higher than normal, due to the minute thickness of the layer: see Ref. 13).

The ring-shaped area of minimal layer thickness opposing the flow of liquid was referred to, in our experiments, as the barrier.

The mechanism of barrier formation apparently consists in the following. Consider the case of a bubble acted upon by a force N (such as the force of ejection causing the bubble to rise in a liquid). Let us assume that the bubble moves as a unit and, on striking a solid surface, becomes partially flattened and stops. The conditions for the outflow of a thin liquid layer between the bubble and the solid surface are most favorable along the circumference bounding the flattened area (Fig. 7), since the free volume is very close. The liquid layer, thinning out rapidly along the periphery, reaches the equilibrium thickness and forms a barrier. As to the layer contained inside the barrier, its location, as explained above, is less favorable for an outflow. Consequently, it retains for a long time its original thickness, which is considerably greater than the equilibrium thickness.

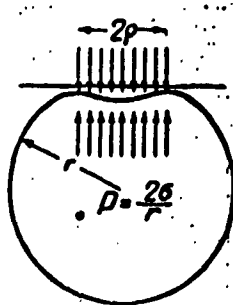


Fig. 8. "Barrier" formation; the wetting film is in a state of nonequilibrium.

In the light of available observations, the proposed theory of barrier formation appears to be correct. The process is confined to the boundaries of circular flattened areas, which have a radius ρ . Such ring-shaped barriers are formed for bubbles of different radii r , scattered freely about the lower surface of a transparent plate (Fig. 8). The ρ values measured with the aid of the interference picture are shown to agree with those obtained by calculation.

To calculate it is sufficient to write down the conditions under which the force of ejection will counterbalance the reaction of a nearly flat solvate layer (Fig. 8) to the capillary pressure K acting upon this layer from inside the bubble. (It is necessary to keep in mind that the curvature of small bubbles is only slightly affected by deformation). We thus obtain:

$$\frac{4}{3} \pi d g r^3 = \frac{2\sigma}{r} \pi \rho^2, \quad (11)$$

where d is the difference between the respective densities of the liquid and the bubble, and g is the acceleration of the force of gravity.

From eq. (8) we have:

$$\rho = \sqrt{\frac{2}{3} \frac{d g}{\sigma} r^3}. \quad (12)$$

In the graph (Fig. 9) the observed ρ values, for bubbles of different radii r , are laid off along the ordinate and the corresponding r^2 values, along the abscissa.

The experimental points fall exactly, or nearly so, on a theoretical curve plotted with the aid of equation (12), into which the follo-

ing given values have been substituted:

$$d = 1.0; \quad g = 981; \quad \delta = 73.$$

The coincidence of the experimental with the calculated curve (12) demonstrates that barrier formation is in effect confined to the periphery of the solvate film, where the surface of the bubble contacts the solid surface. At the same time, direct examination of the interference pattern (see photograph in Fig. 7a) reveals that beyond the barrier the thickness of the liquid layer shows a steep increase.

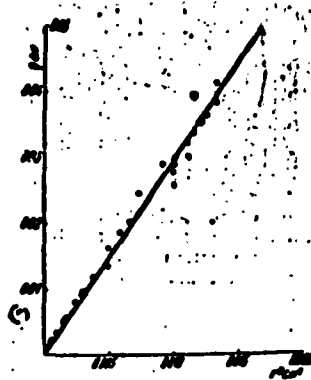


Fig. 9. Dependence of the wetting film radius (calculated line) and the 'barrier' radius (experimental points) on the bubble radius

The formation of a barrier can nevertheless be avoided. If the bubble is slowly pressed against surface A, with the aid of an auxiliary plate B (Fig. 2), no barrier will form. What we observe, instead, is the emergence of a solvate layer of uniform thickness, which will remain unchanged for as long as 24 hours. This thickness is reproducible, with high accuracy, and apparently characterizes a solvate layer at equilibrium with pressure P acting upon it.

In Fig. 10 (see insert) is reproduced one of the many photographs of such an equilibrium layer, obtained in our experiments. The photo-

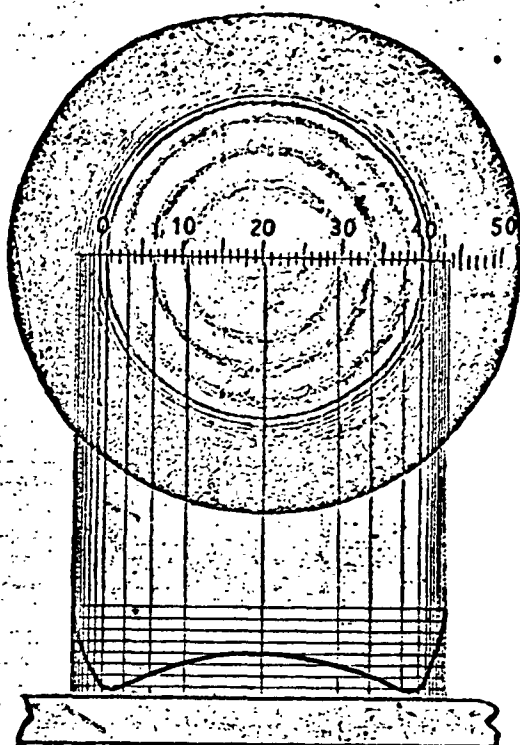


Fig. 7. Microinterferogram of a nonequilibrium wetting film of water; a profile plot of the same film.

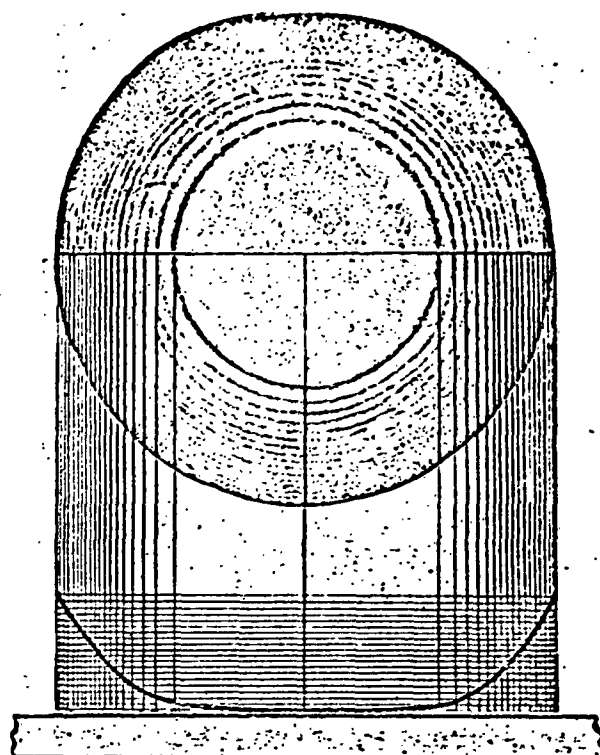


Fig. 10. Microinterferogram of the solvate layer of an equilibrium wetting water film on mica

graph shows clearly that the layer thickness is commensurate with the light wavelength. If it were much smaller, the central portion of the picture would in fact appear bright rather than dark.

In the light of this conclusive visual proof, it can be asserted that the radius of action, for solid surfaces, is not as short as it is often assume to be. (The latter view is based on the existence of monomolecular adsorption layers).

These fundamental findings are of paramount importance for scientific inquiry into molecular forces and surface phenomena.

5. Measurement data on equilibrium thickness of solvate layers

In these measurements, special care was taken to keep the surfaces clean and free of dust. This accounts, in part, for the choice of observation material. Basic measurements were done on mica and glass. Mica surfaces could be made perfectly clean, because the cleaving was done along the cleavage plane, under water. The glass surfaces, melted just before use, were obtained from freshly blown glass bubbles. (A slight correction for surface curvature was introduced into equation 10).



Fig. 11. Isotherm of equation of state of solvate layer. Water on mica.

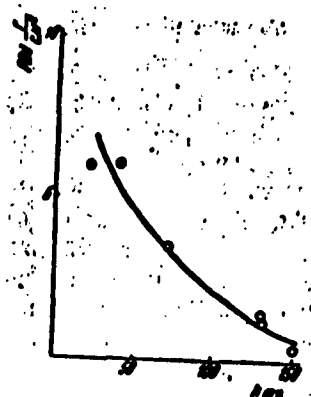


Fig. 12. Isotherm of equation of state of solvate layer. Water on glass.

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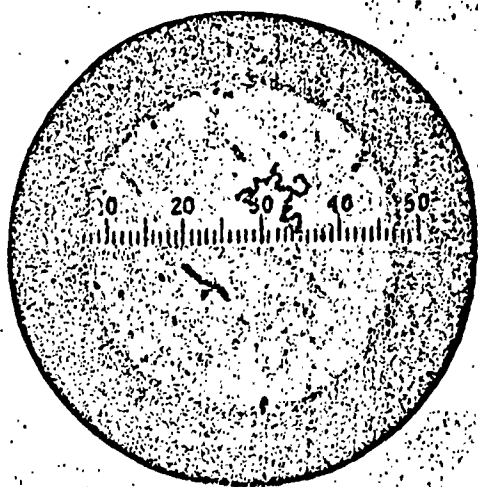


Fig. 14. Desolvating action of electrolytes. The solvate layer is ruptured and a wetting perimeter is formed.

In most of our measurements, hydrogen bubbles were used, formed by electrolysis inside the aqueous medium taken for study. When air bubbles were used instead, this did not affect the results of measurements, except where the solvate layer was "ruptured" and the solid surface became dirty, due to contact with the gaseous phase (i.e., the air bubble).

Double distilled water was always used for measurements.

The graphs in Figs. 11 and 12 demonstrated the dependence of P on h , for double distilled water on mica (Fig. 11) and on glass (Fig. 12). (The reaction was acid, due to the presence of carbon dioxide in the water).

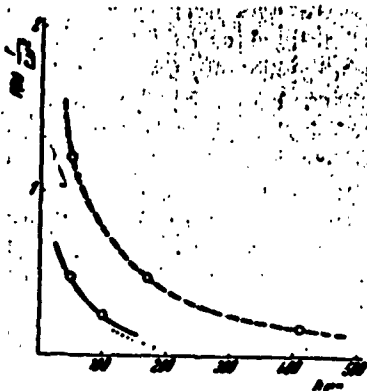


Fig. 13. Effect of adsorption layer on the isotherm of equation of state of the solvate layer. Vaseline oil on steel.

A solvate layer was seen to form also when a glass-alcohol system was applied. It was however too thin to be measured by our visual procedures.

In Fig. 13 measurement data are given for the systems steel surface - pure vaseline oil (solid line); steel surface - vaseline oil containing 1% dissolved oleic acid (dotted line); hexane (curve based on experimental points).

Of particular interest is the effect of electrolytes on the thickness of solvate layers. In the case of monovalent cations the effect is slight, as follows from results obtained for KCl:

Concentration, moles per liter	1.0	0.1	0.01
Pressures, dynes per cm ²	400	400	400
Thickness of solvate layer, mμ	100	50	90

Multivalent cations such as AlCl₃, even in low concentrations (10⁻⁴ N), show strong dehydrating action. As a result, the thickness of solvate layers is reduced to values below the limits of measurement by our method. The contact angle too is changed from zero (pure water) to values ranging 2° - 3°. If the bubble is kept pressed against a glass or mica surface for a certain length of time (varying for different cases), a 'rupture' of the solvate layer develops which spreads very rapidly. Complete wetting is confined eventually to a wetting perimeter often shaped irregularly as a wavy ring (see photograph of interference pattern obtained for this case: Fig. 14, insert).

6. Discussion of measurement errors

We shall now consider the possible (rather limited) criticism of our measurement technique, which gives for solid surfaces a radius of action ($h_0 \approx 10^{-5}$ cm) exceeding considerably the combined thickness of several molecular layers.

It should be pointed out, to begin with, that the method described in this report is superior to those previously used (Ref. 14) in that it does not require perfectly flat surfaces, of the order of 1 cm², but can be used with any sufficiently 'smooth' surface of a much smaller area, ranging 1 mm² to 0.01 mm². It is easy to see, furthermore, that moderate surface curvature, which is much less than the curvature of the bubble pressed against it, should not affect the thickness of the solvate layer coating the surface. Occasionally,

however, the surface curvature is more pronounced. In such cases only, the simultaneous effect of additional Laplacean pressure, exerted by the curved surface separating the solvate layer from the air bubble, may affect the layer thickness.

We have every reason to believe that the surfaces used in our experiments were more than adequate, particularly those obtained from freshly melted glass or the cleavage planes of mica. On some rare occasions, the mica surface in the field of observations had a minute flaw, which we called a 'microterrace'. Such defects were immediately detected, because of the distortions they produced in the interference pattern of the solvate layer.

One of the objection which had to be considered in our old method (Ref. 14) using two solid surfaces separated by a thin liquid layer, was that dust particles settling along the clearance might have an adverse effect on the measurements. In our present study, however, the solvate layer was bounded by one solid surface only, hence this objection was no longer valid.

For one thing, individual dust particles will do no more than create local distortions in the profile of the solvate layer. They cannot affect the average thickness, as measured by the photometric procedure described above. Moreover, local distortions of the interference picture caused by coarser dust particles can be seen under the microscope. The new method, therefore, enabled us to check the surface for the presence of dust. In most of our experiments, the absence of dust particles could be verified on this basis alone. The finer dust particles, on the other hand, are not visible under the microscope. When present in the form of continuous coating, such particles could create an illusion of uniform thickness, with respect to the solvate layer. In our studies, however, the possibility of such dusting was

virtually precluded. It is sufficient to point out that in working with mica, scales of this material were split off under water and the virgin surfaces were examined at once (while still in the same double-distilled water), before they could come in contact with air. The hydrogen bubbles, too, formed in this aqueous medium. In general, research work on surface phenomena would not be possible if under our experimental conditions the solid surface could become densely covered with dust.

It should be pointed out that studying solvate layers bounded on both by liquid (rather than solid) surfaces would be of no advantage, as far as the dust effect was concerned. ⁵ It would in fact render the investigation more difficult, since surfaces of virgin purity would no longer be available. ⁶

Nor could another property of liquid separation surfaces - their perfect flatness - be considered an advantage in our method, since the solid surfaces used were quite satisfactory, in terms of "smoothness" required for our procedure.

As the last possible objection, it may be questioned whether solvate layer thickness yielded by our measurements were in effect equilibrium thicknesses.

The following considerations will suffice to refute this objection.

1) The values obtained for h are easily reproducible.

2) If 'barrier' formation has been prevented (see above), the thickness h (at a constant pressure P) ceases to vary, after the lapse of a certain time interval. The latter amounts to several minutes for water and aqueous solutions, and to about one hour for vaseline oil, whose viscosity is high. In such cases, observations lasting as long as 24 hours fail to disclose any further thinning of the layer. It is concluded that the resistance to the outflow of the liquid, due to viscosity, retards the thinning out of the layer only

by a few minutes (in the case of water). After that an equilibrium is reached between the external pressure acting upon the solvate layer and the disjoining action, whereby the resistance is eliminated. The same thing is demonstrated no less convincingly for solvate layers of vaseline oil. In the course of one-half to one hour the layer thickness may be brought down below that of an aqueous solvate layer after a 24-hour interval, despite the far lower viscosity of water.

3) As the pressure P acting upon a solvate layer increases the thickness h decreases, and vice versa. It would then appear that a layer having a thickness h could be obtained either by thinning out a thicker layer or by thickening a thinner layer (in each case, through appropriate variations of the pressure P). This confirms, at the same time, that the observed thickness correspond to equilibrium values and, furthermore, that the relationships obtained, namely $P = P(h)$ (see graphs in Figs. 10, 11 and 12) represent equations of state (equilibrium isotherms) for the solvate layer.

Thus, all objections to our experimental technique, as discussed above, should be considered invalid.

7. Discussion of results. Effect of adsorption layers on solvation.

The final point to consider is whether the disjoining pressure P of the solvate water (for the case of water) could be identified with the repulsion of ions carrying charges of the same sign, which form the outer diffuse ionic layers adjacent to the two boundary separation surfaces on either side of the layer. Measurements of the ζ -potential indicate, in fact, that air bubbles as well as glass and mica surfaces are charged negatively in water. The diffuse outer membranes of both separation surfaces are thus found to be composed of ions carrying charges of the same (positive) charge.

It is easy to see - as shown also in the quantitative theory of interaction of two surfaces ⁷ carrying diffuse ionic layers (Ref. 15), developed by B. Deryagin - that such repulsion becomes undetectable at a distance several times greater than the effective thickness of the diffuse layers d . For monovalent electrolytes, this distance is equal to

$$d = 0.3 \cdot 10^{-7} \frac{1}{\sqrt{c}}, \quad (13)$$

where c is concentration, in moles per liter.

For pure water, the value d may, in effect, be of the order of

$$10^{-4} - 10^{-3} \text{ cm.}$$

Thus, in the case of pure water, the disjoining action can be ascribed, at least in part, to the presence of ion sheaths.

We have seen, however, that monovalent electrolytes (KCl), in concentrations up to normal, do not substantially alter the order of magnitude of those h values at which the disjoining action is still perceptible. Thickness d , on the other hand, decreases in this case, to a value of $0.3 \cdot 10^{-7}$ am, in accordance with eq. (13). It follows that the disjoining effect cannot, under the circumstances, be traced back to repulsion of two identically charged ionic layers. The existence of cleavage in nonaqueous layers (vaseline oil, hexane) further indicates that the nature of this effect must be a very different one.

From measurements involving multivalent cations, it is seen however that the ions apparently are adsorbed by the solid surface, causing its dehydration, and may thus indirectly affect to a very great extent both the thickness of solvate layers and their cleaving action.

Further evidence is furnished by measurements conducted on solutions of oleic acids in vaseline oil, indicating that adsorption of surface-active molecules (on steel) may likewise have a strong effect. In this

case again the thickness and the cleaving effect of solvate layers are increased; or, to put it another way, the solvation, as this term is interpreted here, becomes intensified.

The above testifies also to the correctness of a hypothesis advanced by B. Deryagin as far back as 1933 (Ref. 16). According to this view, adsorption layers may affect the adjacent liquid layers, by increasing the thickness of the lyospheres or of the solvate layers. This, in turn, influences the related phenomena, above all the stability of colloids and dispersoids, which depends on the disjoining effect of solvate layers. A more detailed discussion of this relationship will be found in sections 8 and 9.

We thus arrive at an explanation (first proposed by B. Deryagin, in the same year 1933: see Ref. 16) of the mechanism underlying the effect of adsorption layers on the stability of disperse systems (for instance, suspensions). P. Rebinder and his followers (Ref. 17) used ample experimental material to investigate this effect.

The basic point, in our explanation, is that adsorption layers have no direct effect on stability but influence it indirectly, through solvate layers, whose essential properties (equation of state) they affect. The same interpretation may be applied to other effects attributable to adsorption layers, such as their influence upon the volume of precipitates, the swelling of colloids, or the dispersive power.

In a like manner, the effect of adsorption layers on stability may apparently be related to lyophilic colloids. The part played by the "third component" in ensuring the high stability of lyophiles will thus be elucidated. In Section 9 we shall show that the above theory can be expressed in the form of a quantitative relationship. On this basis, the stability of colloids and dispersoids will be treated mathematically, in a way consistent with experimental findings.

8. Interaction of spherical micelles in a dispersion medium:

theoretical analysis ⁸

The disjoining action of solvate layers, in those specific manifestations which are the subject of our experimental study, is associated with plane-parallelism, i.e., with uniform thickness of these layers. The science of colloids, on the other hand, is concerned primarily with the effect of cleavage on forces emerging as colloidal particles approach one another. But this is the case of a liquid layer of non-uniform thickness enclosed between two convex surfaces (Fig. 17).

To pass from the first case to the second, it is however sufficient to use an earlier formula derived by B. Deryagin for a general case in his theory of particle adhesion (Ref. 18). This formula, in our estimation, is of major significance for the problem of colloid stability as well as many other important problem of the theory of colloids. We shall therefore show here the derivation of the formula for the simple case of two spherical particles.

Let us begin by considering, once more, the case of a thin liquid layer of uniform thickness. The very existence of disjoining action indicates that isothermal thinning of the layer, from ∞ to h , being a reversible process, consumes energy, which per unit area amounts to

$$F(h) = \int_h^{\infty} P(h) dh. \quad (14)$$

We shall assume that the energy to be expended has been stored as additional free energy of a liquid layer, and is consequently equal to $F(h)$. We shall call function $F(h)$ the characteristic function of the liquid layer, since it determines the equation of state $P = P(h)$ of this layer. On the other hand, $F(h)$ can be obtained directly from our experimental data for $P(h)$ by the method of graphic integration.

It is further assumed that when $h = \infty$, the liquid layer is acted upon by surface energies σ of the two separation surfaces (taken to be identical) by which it is bounded. Together with the additional free energy, the total free energy, for a layer of small thickness h , will be expressed as

$$W(h) = 2\sigma + F(h). \quad (15)$$

At $h = 0$ the layer disappears, along with the bounding separation surfaces. We now have

$$0 = 2\sigma + F(0),$$

hence,

$$F(0) = -2\sigma, \quad (16)$$

Since for $h = \infty$, $F(h) = 0$, it follows that in the case of a liquid layer enclosed between two identical surfaces, the disjoining action, which is equal to

$$P(h) = -F'(h). \quad (17)$$

is either negative for any h value -- that is, the layer tends to decrease spontaneously in thickness (Figs. 15 and 16, curves 1) --

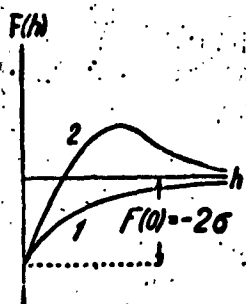


Fig. 15. Two basic shapes of the characteristic function of a thin layer of liquid enclosed between two identical surfaces

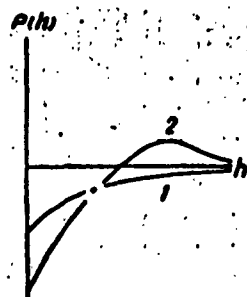


Fig. 16. Two basic shapes of an isotherm of the equation of state for a thin layer enclosed between two identical surfaces

or else curves $F(h)$ and $P(h)$ intersect the abscissas (Figs. 15 and 16, curves 2), so that P is negative for sufficiently small h values but becomes positive when these values are large.

We see, therefore, that a disjoining action between two identical surfaces will exist only if the conditions of the second case are satisfied.

This observation is of importance for the problem of colloid stability, but it will not affect the formulas derived subsequently in this section. The only fact of any importance to us, at the moment, is that the expression for the free energy of a system containing a thin liquid layer of thickness h includes a term

$$U = S \cdot F(h), \quad (18)$$

which is a function of h , where S is the area of the layer.

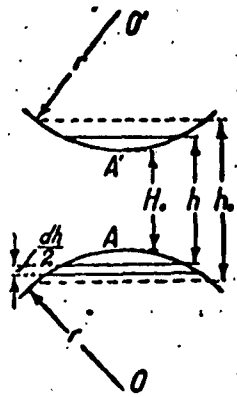


Fig. 17. The force of interaction of two spherical particles in a dispersion medium.

We shall next consider the case of two spherical particles of radius r , separated by a liquid layer of nonuniform thickness (Fig. 17).

In this case, the nonuniform layer thickness changes slowly from point to point, since the layer is bound everywhere by nearly parallel portions of two surfaces. By generalizing eq. (18), the additional energy of this layer (at least where its thickness is less than h_0 , which is the radius of surface molecular action) ¹⁰ may at the first approximation be considered equal to

$$U = \int F(h) dS, \quad (19)$$

where the integral is taken over one of the two surfaces, bounding the thin layer on one side.

To justify the use of this approximation in the case to be considered, where a liquid layer is enclosed between two spheres of radius r , it is necessary that r be large in comparison with h_0 . The portions of the spherical surfaces separated by distances smaller than h_0 will then be not too distant from areas most close to one another (i.e., from points A and A' in Fig. 17). In other words, these portions will be 'nearly parallel' to each other. (The normals to areas facing each other will intersect at very small angles).

When applied to the case of two spheres, eq. (19) can be simplified by use of the geometric theorem concerning zone areas measured upon a spherical surface. The latter is divided into zones by planes perpendicular to a straight line connecting the center O of the sphere with the center O' of another sphere. Taking dS in eq. (19) equal to the area of one such zone, we can write, in accordance with the above theorem:

$$dS = 2\pi r \frac{dh}{2},$$

Accordingly, integral (19) assumes the form

$$U = \pi r \int_{H_0}^{\infty} F(h) dh. \quad (20)$$

The upper limit can be taken equal to infinity without detracting from the mathematical precision, because $F(h)$ will equal zero beginning with small h values.

The expression derived for U apparently represents the potential energy of interaction of two spheres, ¹¹ which amounts to the work that must be expended in the (reversible) motion of these bodies as the distance between them is reduced from infinity to H_0 .

From eq. (20) the force of repulsion N acting between the spheres is determined, in accordance with the well-known theorem of mechanics:

$$N = - \frac{\partial U}{\partial H_0} = \pi r F(H_0) = \pi r \int_{H_0}^{\infty} F(h) dh. \quad (21)$$

It follows from the above that the force of interaction existing between colloidal particles of any radius (not excessively small) separated by any distance, can be determined by graphic integration of a $P(h)$ curve plotted directly from experimental data.

As pointed out earlier (see Section 1), the widely accepted explanation relating the stability of lyophilic colloids to a 'washout' of the solvate layer, is not valid. It is, in fact, immediately evident from equation (21), and even more so from Fig. 15, that this is not so. The 'washout' of a solvate layer is expressed graphically by a gradual decline of curve $F(h)$, and also $P(h)$, with increasing values of h . At a given ϕ value, the 'washout' in itself will not decrease particle interaction (i.e., repulsion or attraction, depending on the

sign of $F(h)$ which is negative in the case of attraction). Rather, the interaction is intensified, because the radius of action, for the forces concerned, becomes lengthened. What accounts for this is that the decrease of $F(h)$ with increasing h values is slowed down in this case.

The maximum value of the force of interaction, according to eq. (15) and (21), will depend only on surface energy σ available along the boundary line separating the particle from the dispersion medium, and will be always negative, if σ is in every case assumed to be positive.

Therefore, a decrease in the action of forces of adhesion, which leads to the stabilization of the system, cannot be related to a 'washout' of the solvate layer. More likely, it depends (at a given σ) on the change of sign for values $F(h)$. When the respective curve (such as curve 2 plotted in Fig. 15) intersects the abscissa, a portion of it becomes positive, which corresponds to a decrease in activity.

To put it another way, stabilization of colloids is ensured by an energy barrier that must be overcome as two particles approach each other; i.e., some activation energy must be available to these particles. In this case both the motion of particles drawing closer to each other, and subsequently their adhesion, will be obstructed by a kind of activation energy, with the result that a degree of aggregative stability will have been achieved. In the next Section the idea will be elaborated and subjected to rigorous mathematic treatment.

9. Theory of slow coagulation and of stability of colloids

In the classic theory of rapid coagulation, developed by Smolukhovsky, coagulation velocity v_0 , equal to the decrease in the number of particles per unit of time, is expressed by the following relationship:

$$v_0 = 8\pi Drc_0^2, \quad (22)$$

where c_0 is partial concentration (in cm^3); D is the coefficient of particle diffusion; and r is the radius of particles.

In deriving equation (22) a condition is assumed that characterizes rapid coagulation. When $H_0 = 0$, the particles, at each collision, are assumed to adhere to each other under the action of forces of molecular attraction. When $H_0 > 0$, on the other hand, there are presumably no forces acting between the particles. In other words, the radius of action, for surface forces, including the forces of adhesion, is taken to equal zero. At the same time, the probability of adhesion, at each collision - i.e., the efficiency of the acting forces - is assumed equal to unity.

That the second assumption is correct, was confirmed by direct observation (Ref. 19) for aerosols whose $cr \approx 10^{-1} - 10^{-4}$ cm.

It was shown theoretically (Ref. 20) that in the case of an aqueous dispersion medium, the efficiency of a single collision must be much less than unity if coagulation is to be slow; i.e., if its rate is to be appreciably lower than the value v_0 obtained from eq. (22).

This refutes the view held by Smolukhovsky, who thought that the velocity of slow coagulation must be proportional to the efficiency of collisions, as defined above.

On the other hand, the very concept of 'probability of adhesion' at collision, even when associated with a correct approach to the problem of coagulation, testifies to our ignorance of the cause, or the mechanism, of colloid stability. It means, also, that no effort is made to develop a theory of stability, inasmuch as nothing is said about the possible factors controlling the probability of adhesion.

Moreover, if the particles are sufficiently large in comparison with molecular dimensions, it can hardly be expected that, at $H_0 = 0$, 'chance factors' might be able to hinder adhesion, reducing efficiency at collision to a level appreciably below unity.

Our purpose, however, is to develop a theory of slow coagulation as related to stability of colloids. With this in mind, we shall assume, for the case where $H_0 = 0$, that the particles always become aggregated (i.e., efficiency at collision equals unity). At the same time, the radius of surface action will no longer be assumed to equal zero. In estimating particle interaction, we shall make use of results obtained in the preceding Section.

Thus, if the act of collision is identified with the case where $H_0 = 0$, collision efficiency will equal unity. If, however, the act of collision is identified with the case where the particles are separated by a clearance $H_0 = h_0$, collision efficiency may be considerably less than unity, under conditions of "cleavage". The probability of adhesion can be precalculated, for this case, on the basis of the law of particle interaction.

To calculate the velocity v of slow coagulation, taking account of particle interaction, we shall use the formula

$$v = \frac{16\pi D_0^2}{\int_0^\infty \frac{1}{\left(r + \frac{1}{2}H_0\right)^2} e^{-\frac{U(H_0)}{kT}} dH_0} \quad (23)$$

where $U(H_0)$ is the potential energy of interaction between two particles, which equals the energy expended as they move toward each other, from an infinite distance to a distance H_0 ; k is the Boltzmann constant; and T is the absolute temperature.

Formula (21) was derived (Ref. 21) as a generalization of Smolukhovsky's equation (22) for the case of interacting particles (charged particles of aerosols).

For our purposes, the terms 'stability' of a colloidal system is best interpreted as a value L which is the reciprocal of coagulation velocity v :

$$L = \frac{1}{v}, \quad (24)$$

From eq. (22), (23) and (24) we have:

$$\frac{L-L_0}{L} = r \int_0^{\infty} \left[e^{\frac{U(H_0)}{kT}} - 1 \right] \frac{dH_0}{\left(r + \frac{H_0}{2}\right)^2}. \quad (25)$$

For the case where $U(H_0) > 0$, the above expression signifies an increase in the stability of the system, associated with cleavage and the characteristic function:

$$U(H_0) = \int_{H_0}^{\infty} N(H_0) dH_0 = \pi r \int_{H_0}^{\infty} dH_0 \int_{H_0}^{\infty} P(H_0) dH_0. \quad (26)$$

or, integrating in parts:

$$U(H_0) = \pi r \int_{H_0}^{\infty} P(\zeta) (\zeta - H_0) d\zeta. \quad (27)$$

By treating graphically the experimental curve $P(H_0)$, we can now determine $U(H_0)$ for different r values, and next the value

$$\frac{L-L_0}{L_0}.$$

We shall cite here the results of such calculations obtained for a water-glass system.

A distinction must first be made however, insofar as the disjoining effect is concerned, between two cases. In the first case, a thin liquid layer is bounded by a solid body on the one side and by gas on the other. In the second, which is the case in our experiments, the same type of layer is enclosed between two identical solid bodies. The cleaving action manifested in the latter case is the only one that is of importance for the theory of coagulation.

To complete our calculations, we shall assume the disjoining action in the second case to be twice as strong as in the first. This means that the respective functions $P'(h)$ and $F'(h)$ can be obtained for the second case by doubling the $P(h)$ and $F(h)$ values, based on direct measurements, relating to the first case. Such an assumption cannot of course be considered correct, except as a rough approximation. Strictly speaking, it is justified only as an aid in computing at least the order of magnitude, for the stabilizing action of solvate layers.

Function $U(H_0)$ for the value $r = 10^{-5}$ cm is plotted in Fig. 18, by use of eq. (26), after doubling the function values, as indicated above.

It is seen from the graph in Fig. 18 that for $H_0 < 10^{-4}$ cm $U > 7 \cdot 10^{-12}$. Since at room temperature $kT \approx 4 \cdot 10^{-16}$, it follows that for $H_0 < 10^{-4}$ cm the ratio $\frac{U}{kT}$ will be greater than 175. In this case, for $r = 10^{-5}$ cm, expression (25) will yield the inequality

$$\frac{L}{L_0} > \frac{L - L_0}{L_0} > 10^{10}. \quad (28)$$

In pure water the system, as follows from the above, will be absolutely stable, or nearly so, at $r > 10^{-5}$ cm.

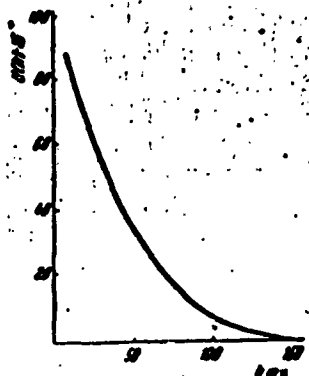


Fig. 18. Potential interaction energy of mutual repulsion of two glass spheres, $r = 10^{-5}$ cm, in water, as a function of distance separating their surfaces. The energy values were computed by recalculating an isotherm of the equation of state, obtained experimentally for a water film on glass.

It will be noted that for lesser r values our calculations become inaccurate, since they are based on a formula that gives sufficiently close approximation only for r values large enough as compared with h_0 . This latter value, according to our measurements, is of the order $10^{-6} - 10^{-5}$ cm.

CONCLUSIONS

1. The current concepts relating to surface solvation are not clearly defined, nor do they furnish a basis for quantitative evaluation. The lack of a direct experimental approach is responsible for the dearth of information on the properties and thickness of solvate layers.

2. The most important property of such layers should be identified with the disjoining action exhibited by a thin film of liquid separating two phases (two micelles; also, a solid or liquid phase and a gas bubble).

3. Quantitatively, this property is characterized by the dependence of equilibrium disjoining pressure P on thickness h of a plane-parallel layer. Function $P = f(h)$ represents an isotherm of the equation of state for this layer.

4. The proposed definition of solvation is consistent with conventional views relating solvation to intense molecular interaction of a disperse medium with disperse phase. This is demonstrated by calculations in which molecular interaction is assumed to be additive.

5. A method for deriving the equation of state for a solvate layer has been developed by the authors. When applied to a wetting film between a bubble and a solvated surface, it offers many advantages over the procedure described in previous reports of the present series -- among these simplicity, ready elimination of the dust effect, the possibility of working with small surface areas, etc.

6. When a gas bubble is pressed quickly against a solid surface, a wetting film of nonuniform thickness corresponding to a state of non-equilibrium is formed. The film grows thinner toward the edges.

7. If pressure is applied slowly, a film of uniform thickness corresponding to a state of equilibrium will form after some lapse of time.

8. The film thickness is a decreasing function of pressure exerted upon the film by the gas contained in the bubble.

9. The above method was used to derive equations of state $P = p(h)$ for a water film on glass and mica, and for a film of vaseline oil on steel.

10. When pressure P is of the order of 500 dynes/cm^2 , the film has a thickness of about 10^{-5} to $3 \cdot 10^{-5}$ cm. The surface effect is thus seen to penetrate into the adjacent liquid layer, to a depth of many molecular layers. This contradicts some of the views frequently voiced in

the literature.

11. Addition of KCl to water, even in normal concentration, does not affect the thickness of a solvate layer. This indicates that the disjoining action cannot be identified solely with the mutual repulsion of diffuse ion sheaths on both surfaces of the solvate film.

12. Trivalent cations such as AlCl_3 exert a strong desolvating action, whereby the wetting film thickness is reduced to an extremely small value and complete wetting is limited to an incomplete process (contact angle, $2-3^\circ$).

13. Addition of oleic acid to vaseline oil increases the thickness of an oil film on steel to several times its original value. Thus, direct experimentation confirms the hypothesis advanced back in 1933 by B. Deryagin, who believed that adsorption layers influence both the thickness and disjoining action of solvate layers, thereby intensifying solvation.

14. A simple mathematic conversion makes it possible to express the disjoining action exerted by a uniformly thick layer of the disperse phase in terms of r and the function $P(h)$. In this case the dispersion medium separates two adjacent spherical particles, or radius r (not excessively small). Function $P(h)$ expresses the cleaving action of a layer having uniform thickness. The force of repulsion acting between particles that are not too small was found to be directly proportional to their radius.

15. A mathematical theory of slow coagulation related to stability of colloids and dispersoids was developed, based on the equation for the interaction of adjacent particles. According to this theory, stability is determined by the disjoining action, since the latter causes the emergence of an energy barrier which hinders the contact and adhesion of particles.

16. Substitution of experimental values into theoretical expressions derived by the authors reveals that the proposed concept of disjoining action offers an adequate quantitative interpretation of the factors determining the stability of colloids and dispersoids. The theory is consistent with experimental results obtained for particles whose radius is greater than 10^{-5} cm, but cannot be applied to particles of lesser size (see Paragraph 14).

17. The proposed theory accounts for the effect of adsorption layers - the third component - on the stability of colloids. These layers are shown to intensify the disjoining action of diffuse solvate layers, thus influencing stability. The mechanism underlying the action of adsorption layers, as suggested back in 1933 by B. Deryagin, clarifies the influence of adsorption layers on the stability of suspensions investigated by P. Rebinder and coworkers. It accounts, furthermore, for a number of other effects exhibited by surface-active substances (adsorptive lowering of hardness, investigated by the same authors; the lubricating effect, etc.).

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Laboratory of Thin Films
Department of the Physical
Chemistry of Disperse Sys-
tems and Surface Phenomena
Institute of Electrochemistry
and Colloids
Academy of Sciences USSR

FOOTNOTES

1. Reported at the Conference of the Chemistry Group, Academy of Sciences USSR, on lyophilic colloids, May 9, 1937.
2. Previous reports: I. B. Deryagin. Zhurnal fizicheskoy khimii, 3, 29 (1932); Zs. f. Phys., 34, 657 (1933); II. B. Deryagin. Zhurnal fizicheskoy khimii, 5, 379 (1934); Phys. Zs. d. Sowietunion, 4, 431 (1933); III. B. Deryagin and E. Obukhov. Zhurnal kolloidnoy khimii, 1, 385 (1935); Acta Physicochemica URSS, 5, 1 (1936); IV. B. Deryagin and M. Kusakov. Izvestiya Akademii Nauk SSSR, Seriya khimicheskaya, 741 (1936).
3. The above assumption, if accepted, would limit considerably the general applicability of the theory, since it leaves out of consideration that the energy of interaction between two molecules may also depend on their orientation. (This is especially clear in the case of dipole molecules). Such orientation is influenced by other molecules, particularly the neighboring ones. The existence of distinct molecule orientation patterns has been proven, and shown to be a major factor in the disjoining action. A portion of the free energy possessed by a two-micelle system depends on the diffuse ionic layers, and cannot be estimated by the Laplace-Gauss method. For this reason, the subsequent discussion will not be in any way restricted to such conditions as are imposed by this assumption. Its purpose was merely to demonstrate that a relationship exists between the disjoining action and the intensity of interaction of the solvating with the solvated phases.
4. Studies on a wetting film were also conducted by Academician A.N. Frumkin and coworkers (Ref. 11), but in their case it was a film formed between a hydrogen bubble and mercury. The thicknesses were not measured directly, but were determined by an interesting indirect method.

The main distinction between these experiments and ours consisted in the following. Our studies were concerned principally with the equation of state for a wetting film - i.e., with the disjoining effect as a function of thickness (under conditions of complete wetting). A.N. Frumkin and coworkers, on the other hand, were interested mainly in the thickness of the wetting film and the contact angle formed by the bubble, under conditions of incomplete wetting. Their data were obtained for varying values of mercury polarization, irrespective of the pressure within the bubble.

It might be added that the thicknesses obtained for a water film on mercury were considerably lower than in our studies, reaching a value of 10 m μ only in cases of strong mercury polarization. This is understandable, since the nature of a mercury surface is quite different from that of hydrophilic mica, or glass. The need for strong polarization suggests further that the nature of phenomena subjected to inves-

tigation was not identical in the two cases.

5. Such a study was undertaken by one of us, in collaboration with L.N. Bronstein, at the All-Union Institute for Experimental Medicine, Department of Biophysics.

6. Thus, the objection raised by Professor S.M. Lipatov during a discussion of our report is fully refuted. In the opinion of Professor Lipatov, the validity of results obtained in this type of experiments on solid surfaces may be questioned in all cases.

7. See the report by B. Deryagin, published in this issue.

8. Theoretical calculations, in this and the following sections, have been performed by B. Deryagin.

9. From eq. (15) it is seen that function $F(h)$ indicates the extent of deviation from additivity, for surface energies possessed by separation surfaces bounding a thin liquid layer.

10. The radius of surface molecular action will be taken to mean that thickness of the layer which, if exceeded, will render $F(h)$ and $P(h)$ negligibly small.

11. More exactly, the additional free energy possessed by the liquid layer separating these spheres.

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3. Extensive studies of bound water have been carried out by A.V. Dumansky and coworkers. See, for instance: A. Dumansky. Izvestiya Gosudarstvennogo Issledovatel'skogo Instituta Kolloidnoy Khimii (Bulletin of the State Research Institute for Colloidal Chemistry), 2, 3 (1934).; A. Dumansky and A. Dumanskaya, ibidem, p. 43.; A. Dumansky and M. Čapek, ibidem, p. 56; Z. Chesheva, ibidem, p. 20.
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